Summary

Toxicity of Pb has been recognized since Antiquity. It has no known biological benefit to humans and poisoning commonly occurs after prolonged exposure to Pb or its compounds. The groups most at risk for the adverse effects of Pb are pregnant woman, breast-feeding women and young children. Even at low exposure levels, the effects of Pb on children include impairment of normal neurological development leading to learning and reasoning difficulties, retardation of physical development, hearing loss, hyperactivity, and reduced attention span.

Starting in the 1970s, health concerns led to a series of worldwide measures to reduce the input of anthropogenic Pb to the environment. In developed countries worldwide the usage of Pb based paint and Pb solder in water pipes and food cans was prohibited, metallic Pb in shot cartridges was banned and the Pb content in PVC and gasoline was reduced significantly. Although various measures have been taken and numerous polluted sites have been remediated, thousands of sites worldwide are still polluted with Pb. In addition, Pb products are still manufactured and used (e.g., building material (sheeting and gutter material), cable sheating, car batteries, Pb crystal glass, ammunition, radiation protection and solders), and can enter the environment after use.

The goals of this thesis were to map Pb distribution in rural and urban soils in The Netherlands, to unravel Pb sources and to obtain information about the mobility and oral bioaccessibility of anthropogenic Pb in the Dutch environment. This study is carried out in The Netherlands because it is one of the most densely populated countries in the world with several thousand registered Pb polluted sites. In several parts of The Netherlands exposure to Pb, especially in soils in cities and villages with a long habitation history, remains a serious risk.

Based on measurements of Pb content alone, it is often difficult – if not impossible – to determine the cause of the elevated Pb content and to distinguish between natural and anthropogenic origins. This thesis investigated the use of Pb isotopes to distinguish natural from anthropogenic Pb and to unravel anthropogenic Pb sources. Lead consists of four stable isotopes - ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb - of which ^{204}Pb is non-radiogenic and ^{206}Pb, ^{207}Pb and ^{208}Pb are formed by the radioactive decay of ^{238}U, ^{235}U and ^{232}Th respectively. Due to the analytical technique applied in this study, ^{204}Pb could not be determined quantitatively. Lead ores, used to manufacture Pb-base products, often have characteristic Pb isotope ratios (e.g., ^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb and ^{206}Pb/^{208}Pb). These ratios mainly depend on the initial U/Pb and Th/Pb ratios and geological age of the source rocks from which Pb was derived during ore formation. In general it can be stated that the older the Pb ore, the less radiogenic the isotopic composition and the lower the ^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb and ^{206}Pb/^{208}Pb ratios. As Pb isotopes do no fractionate measurably during ore processing (e.g., mining and smelting), the Pb isotope ratios of the Pb containing products (anthropogenic Pb) are similar to the isotopic ratios of the ores from which they are made.

This thesis shows that the Pb isotope composition of anthropogenic Pb in rural, urban and roadside soils in The Netherlands differs clearly from lithologically inherited (natural) Pb in Dutch soils. The average Pb isotope composition of lithologically inherited Pb in Dutch soils equals present day common Pb due to the presence of a mixture of Pb, U and Th containing minerals. In time the Pb isotope composition of lithologically inherited Pb will keep changing

(become more radiogenic) due to the ongoing radioactive decay of ^{238}U, ^{235}U and ^{232}Th present in U and Th bearing minerals in natural Dutch soils. The Pb isotope composition of anthropogenic Pb in Dutch soils is in general less radiogenic (lower $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios) than lithologically inherited Pb. Due to the (near) absence of ^{238}U, ^{235}U and ^{232}Th, the Pb isotope composition of anthropogenic Pb still reflects the Pb isotope composition of the Pb ores (mainly galena) from which they were made. As these ores are millions of years old, the Pb isotope composition of anthropogenic Pb clearly differs from lithologically inherited Pb.

Lithologically inherited Pb in the four main lithologies distinguished – sand, clay, peat and loess – has distinct Pb isotope signatures. Clays have higher average $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios than sands. Peats show Pb isotope ratios that match both sands and clays due to the presence of Pb containing sand and clay mineral in peats. Loess shows the highest average $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios of the four distinguished lithologies. The observed variation is primarily explained by the textural and mineralogical variation within Dutch sedimentary soils, with Al and Zr content representing useful predictors for the observed Pb isotope variability. The Zr content is a proxy of the proportion of U and/or Th containing primary minerals that on average have more radiogenic Pb isotope compositions. The U/Th ratio of zircons is generally much higher than that in the bulk rocks, which explains the trend in Dutch sedimentary soils of lower contributions of ^{208}Pb, relative to ^{206}Pb, with higher Zr content. The Al content represents the proportion of secondary clay minerals that incorporate the more recently formed radiogenic Pb that is relatively low in ^{207}Pb compared with ^{206}Pb and ^{208}Pb. The different, apparently older, isotopic signature of the sands compared with the clays, can thus be attributed to the lower proportion of radiogenic Pb from secondary minerals (clays) as well as a broader range towards lower Zr contents. The more radiogenic signature of the loess samples, compared with the sands and clays, is only partly explained by their relatively high Al and Zr content.

Since the isotopic composition of natural and anthropogenic Pb differs substantially in Dutch soils, they were used to identify anthropogenic Pb sources. Nearly all studied rural, urban and roadside topsoils contain anthropogenic Pb, with the highest anthropogenic Pb contents measured in the urban topsoils followed by the roadside topsoils and rural topsoils. The five distinguished land use types – forest, open nature, moor, arable land and grassland – in the rural topsoils have distinct isotopic compositions for anthropogenic Pb. The anthropogenic Pb sources in the topsoils of forest, open nature and moor are most likely atmospherically derived coal/galena, incinerator ashes and gasoline Pb. In contrast, the more radiogenic Pb isotope values of anthropogenic Pb in the topsoils of arable land and grassland is most likely caused by the presence of animal manure and N-P fertilisers.

Several areas were observed with notably high anthropogenic Pb contents in the rural topsoil. The largest area is the Randstad area which has the highest population and traffic density and hosts several long-running waste incinerators and a considerable fraction of the Dutch chemical industry. Two other areas are located near the Dutch-German and Dutch-Belgian border and are most likely influenced by German and Belgian chemical industries. The lowest anthropogenic Pb contents in rural topsoil were measured in the coastal dunes and southern, central and northern forests where population, traffic and chemical industry density is low and no fertilisers are applied.

Sandy roadside topsoils have the least radiogenic Pb isotope composition of all studied topsoils in The Netherlands. In addition, a clear decrease in anthropogenic Pb content was observed with increasing distance from the highways. Anthropogenic Pb in the roadside soils is mainly derived from gasoline Pb and occurs to a depth of approximately 15 cm. Lead is shown to be associated with organic matter. Due to the low pH and negligible binding capacity of the studied roadside soils at depths >15 cm, anthropogenic Pb migrated towards groundwater. This is established by the Pb isotope composition of the groundwater. Assuming that the downward Pb flux was constant over time, it is calculated that 35-90% of the atmospherically delivered anthropogenic Pb has migrated to groundwater.

Urban lake sediments provided temporal information on the variation in atmospheric Pb deposition and changes in atmospheric anthropogenic Pb sources between 1942 and 2002 A.D. in The Netherlands. The rise and fall of leaded gasoline is clearly reflected in reconstructed atmospheric deposition rates. The lake sediments show that measures taken to improve air Pb quality have been successful. After the ban of leaded gasoline, late 1970s/early1980s, atmospheric Pb deposition rates decreased rapidly and the relative contributions of incinerator ash (industrial Pb) and coal/galena increased sharply. Despite the mitigation measures, atmospheric Pb deposition rates in the Dutch urban lakes are still significantly higher than the European background fluxes. This is attributed to the proximity to major highways and industrial activities. Annual atmospheric Pb deposition rates inferred from the lake sediments record a clear relationship with nearby measured annual mean air Pb concentrations. Based on this relationship it was estimated that air Pb concentrations between 1942 and 2002 A.D. never exceeded the European limit value of 500 ng/m^3.

Contrary to the rural and roadside topsoils, atmospheric Pb is not the dominant anthropogenic Pb source in urban topsoils. In ~75% of the urban soils the source of Pb pollution was a mixture of glazed potsherds, sherds of glazed roof tiles, building remnants (Pb sheets), metal slag, Pb-based paint flakes and coal ashes. In the other ~25% of the soils, Pb isotope analysis suggests that Pb pollution was caused by incinerator ash and/or gasoline Pb suggesting atmospheric deposition as the major source. Lead in the anthropogenic Pb sources predominantly (~80%) originates from Belgium, German, British or Irish mines. Since the Pb isotope compositions of the various mines overlap, it was not possible to ascribe a single origin for most Pb sources. No clear differences were observed in the Pb isotope ratios of urban soils polluted in Roman, Medieval or Modern times.

In human risk assessment, ingestion of soil is considered a major route of toxic Pb exposure. This applies especially to young children due to their frequent hand-to-mouth behaviour. The relative oral bioaccessibility (i.e. the maximum bioavailability) – determined with an *in vitro* test – of soils polluted with various Pb sources (e.g., Pb bullets and pellets, car battery Pb, gasoline Pb, city waste and diffuse Pb) varied from 0.5% to 79%. The variance is explained by 1) the chemical composition of the anthropogenic Pb source and its solubility, 2) the specific reactive surface of Pb artifacts in the soils and 3) soil type (e.g., sandy or clayey soils with and without calcium carbonate), and capacity to form secondary phases. Oral bioaccessibility was significantly correlated with pH, organic matter and reactive Fe. These results indicate that soil characteristics play an important role in the oral bioaccessibility of lead in polluted soils. Instead of basing human risk assessment solely on total Pb contents we propose to incorporate *in vitro* bioaccessibility tests, taking factors such as soil pH, organic matter content and reactive iron content into account.